

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO RUST-PROOFING PAINT

(71) We, KANSAI PAINT COMPANY, LIMITED, of 365 Kanzaki, Amagasaki-shi, Hyogo-ken, Japan, a corporation of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a rust-preventing paint for steel, containing a film forming high molecular weight metal containing reaction product.

An object of this invention is to provide a rust-preventing paint which can be easily applied to the surface of steel, so that when rust remains on the surface of the steel, the paint permeates into the layer of rust and when there is no rust on the surface of the steel, the paint adheres securely thereto. As a result, in either case, the paint of the invention can prevent corrosion of the steel in the atmosphere.

For treating rusty steel surfaces, heretofore, an oleo-resinous paint consisting of linseed oil and red lead has been used, but such a paint is insufficient in its rust-preventing effect in polluted air and its speed of drying. The rust-preventing effect of an anticorrosive paint consisting of synthetic resins (for example, red lead paint containing long-chain oil alkyd resins) is also insufficient, because this paint has insufficient ability to permeate into underlying rust and, as a result, the paint does not prevent the growth of rust.

It can be seen that it has previously been very difficult to prepare an effective paint for application to rusty steel surfaces, having the following properties:

- (1) Good wetting, permeation and adherence;
- (2) Good weathering and rust-prevention in polluted air;
- (3) Good workability and rapid drying ability.

It has been discovered that these difficulties may be overcome by using high molecular weight metal containing reaction products as film-forming materials for rust-preventing

paints, which compounds are produced from aliphatic polycarboxylic acids and/or monocarboxylic acids and hydroxides or oxides, of lead, calcium, cobalt, zinc, iron, manganese, nickel, magnesium, barium, cadmium, strontium and chromium, and polyhydric alcohols.

A conventional rust-preventing paint consists of a binder such as processed drying oil, an alkyd resin and/or a phenol resin as a principal film-forming material, and an anti-corrosive pigment selected from red lead, lead powder, lead suboxide, zinc dust, basic lead chromate, and a basic pigment such as zinc oxide and iron oxide powder as an auxiliary pigment. When this paint is applied to the surface of steel, a water-impermeable dry film can be easily formed and, as a result, the pigment in the film forms anti-corrosive substances by electrochemical reaction or by the oxidation and ageing of the film into a passive state, so as to prevent the formation of rust.

In the rust-preventing paint containing a high molecular weight metal containing reaction product of the invention, the oily dispersion of the reaction product employed as a film-forming material has rust-preventing action and, accordingly, the addition of an anti-corrosive pigment is not necessarily required. However, a colouring pigment and extender for general use may be added to the film-forming material to afford a suitable viscosity and fluidity, whereby the paint can be uniformly and thickly applied to a steel material, the film so applied being reinforced and made to afford favourable durability, a desirable colouring also being attainable.

According to one aspect of the present invention, therefore, a rust-preventing paint comprises a film forming high molecular weight metal containing reaction product, having a carboxyl group terminating its structure, the reaction product being obtained by reacting a metal-containing polycarboxylic acid having free carboxyl groups and an acid value of 50—300 with polyhydric alcohol in an amount stoichiometrically less than the carbox-

[Price 25p]

yl groups present in the metal containing polycarboxylic acid, which is itself obtained by reacting an aliphatic polycarboxylic acid having free carboxyl groups with a hydroxide or oxide of lead, calcium, cobalt, zinc, iron, manganese, nickel, magnesium, barium, cadmium, strontium or chromium in an amount stoichiometrically less than the carboxyl groups present in said aliphatic polycarboxylic acid.

A process for the production of a rust-preventing paint, according to another aspect of this invention, comprises:

(1) Reacting less than a stoichiometrically equivalent amount of a reactive metal hydroxide or oxide with an aliphatic polycarboxylic acid having free carboxyl groups, or a mixture obtained by adding an equivalent amount or less of a monocarboxylic acid to such an aliphatic polycarboxylic acid, and heating the resultant mixture to obtain a metal containing polycarboxylic acid having free carboxyl groups and an acid value of 50 to 300; reacting less than a stoichiometrically equivalent amount of a polyhydric alcohol with the free carboxyl groups of the metal containing carboxylic acid, to increase its molecular weight, whereby a high molecular weight metal-containing reaction product having a carboxyl group terminating its structure is synthesized; the thus-obtained reaction product being dissolved, dispersed or suspended in an organic solvent to produce an oily dispersoid;

(2) Next, the above-mentioned oily dispersoid of the high molecular weight reaction product is independently employed as a vehicle, and a paint dryer and, if required, other components are added thereto to produce the desired non-pigmented rust-preventing paint of the invention.

(3) Alternatively, the oily dispersoid of step (1) may be used separately or mixed with some other paint vehicle and also colouring pigments, extenders and additives for paint (that is, auxiliary agents such as dispersing agents, dryers and anti-skinning agents, hereinafter referred to simply as "additives") are added to obtain a mixture which is then treated by a dispersing device such as ball mill or a roller mill to produce the desired rust-preventing paint of this invention. In this case, an anticorrosive pigment may be mixed with the oily dispersoid.

The following components may be used for producing the oily dispersoid of the high molecular weight reaction product of this invention:

(1) The aliphatic polycarboxylic acid preferably is tall oil dimer acid, linseed oil dimer acid, maleic acid or other acids having two carboxyl groups in their molecule.

(2) As the monocarboxylic acid, vegetable oil fatty acids such as linseed oil fatty acid, tall oil fatty acids, rosin acids and benzoic acid may be used.

(3) The polyhydric alcohol may be selected

from, inter alia, glycerol, trimethylolthane, trimethylolpropane and tris(hydroxymethyl)aminomethane.

It is known to use rust-preventing paints, in which an anticorrosive pigment selected from lead pigments such as lead oxide, trilead tetroxide, basic lead chromate and metal powders (for example, zinc dust) is contained, for treatments for preventing the formation of rust on the surface of steel and preventing the influence of polluted air.

On the other hand, a paint prepared by physically suspending hydroxides or oxides of a metal selected from lead, calcium, cobalt, zinc, iron, manganese, nickel, magnesium, barium, cadmium, strontium, chromium, or other metals as a single component or a mixture, in a processed drying oil or other film-forming material has scarcely any rust-preventing effect. Even if some effect is obtained, it is far inferior to that of anticorrosive paints produced from lead pigments and, accordingly, these metal oxides have been merely used as extenders or colouring pigments.

The rust-preventing paint according to the invention has the following excellent characteristic features:

(1) They are dilutable with organic solvents or are capable of forming stable dispersed suspensions therewith;

(2) They can produce flexible films, due to their amorphous nature, which show little change in physical properties with time, and are highly weather-resistant;

(3) Because of the carboxyl groups terminating the high molecular structure, they have favourable wettability, permeability and adhesiveness to the surface of a steel material and the rust remaining thereon and accordingly, are particularly suitable for forming rust-preventing coatings on a rusty surface of steel;

(4) They have excellent durability, because the coated films are difficult to hydrolyse.

(5) They have rapid drying, so that, in a short period after applying the rust-preventing paint of this invention, a synthetic resin type paint can be painted over them and shows excellent adhesiveness to the rust preventing paint;

(6) They have satisfactory storage stability.

As a result, if the rust-preventing paint of this invention is employed for painting steel construction materials, the working property of coating becomes easy. Furthermore, whether or not rust is present on the surface of a steel or even if uneven rust is present on the surface, the paint favourably adheres, wets, permeates thereto and rapidly dries, whereby the durability of the steel material can be considerably increased. Moreover, finishing of the coating can be completed in an early stage and this is useful in practice.

In the following, examples of the rust-preventing paint of the present invention are given, by way of illustration only. In the exam-

ples, amounts are given in parts by weight and percentages by weight unless otherwise stated.

#### EXAMPLE 1

1680 parts (3 moles) of linseed oil dimer  
 5 acid and 560 parts (2 moles) of soybean oil  
 fatty acid were placed in a three-necked flask  
 with a stirrer, thermometer and condenser pro-  
 vided with a branched tube, and heated for  
 30 minutes while stirring, when the tempera-  
 10 ture of the flask contents reached 160°C., 74.1  
 parts (1 mole) of calcium hydroxide were  
 added thereto little by little, and the mixture  
 obtained was reacted for 1 hour while keeping  
 the temperature within the range of  
 15 160°—180°C. Then, 46 parts (0.5 mole) of

glycerol were added, the temperature of the  
 reaction mixture rising to 200°C. for 3 hours;  
 when the total amount of water distilled off  
 reached 63 parts (theoretical value), the heat-  
 ing was stopped to cool the reaction product  
 to about 80°C., when xylene was added to pro-  
 20 duce an oily dispersoid of a high molecular  
 weight calcium product I, having a concentra-  
 tion of 60% by weight.

As shown in the following Table I, to this  
 25 oily dispersoid of product I, a colouring pig-  
 ment and extender were added in a roller mill  
 or ball mill and a dryer and solvent were  
 added, to produce a pigmented rust-preventing  
 30 paint, containing iron oxide as the pigment.

TABLE I

	(parts)
Red iron oxide	8.0
Heavy calcium carbonate	48.0
Oily dispersoid of Product I (solid matter 60%)	39.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	4.0
	<hr/> 100.0

#### EXAMPLES 2 — 11b

Using the same procedure as described in  
 Example 1, instead of 74.1 parts (1 mole) of  
 35 calcium hydroxide, the hydroxides and the  
 basic carbonate of the various metals shown  
 in Table 2 were reacted with the mixture to

produce various oily dispersoids of high  
 pigmented rust-preventing paints of the pre-  
 sent invention were produced by replacing  
 compound I of Table I by the high molecular  
 weight reaction products shown in Table 2, 40

TABLE 2

Example	Reactive Metal Compound	High Molecular Weight Reaction Product	Blending amount (parts)	Total Amount of Distillate Water (parts)
2	Cobalt hydroxide	Product II	92.9	63
3	Zinc hydroxide	Product III	99.4	63
4	Iron hydroxide	Product IV	106.9	81
5	Manganese hydroxide	Product V	88.9	63
6	Nickel hydroxide	Product VI	92.7	63
7	Magnesium hydroxide	Product VII	58.3	63
8	Barium hydroxide	Product VIII	171.3	63
9	Cadmium hydroxide	Product IX	146.4	63
10	Strontium hydroxide	Product X	121.6	63
11a	Chromium hydroxide	Product XIa	103.0	81
11b	Basic lead carbonate	Product XIb	775.7	99

## EXAMPLE 12

630 parts (1.12 moles) of tall oil dimer acid were placed in a three-necked flask with a stirrer, thermometer and condenser provided with branched tubes, heated for 30 minutes while stirring and, when the temperature of the contents had become 160°C., 25.2 parts (0.34 mole) of calcium hydroxide were added little by little, and allowed to react for 1 hour, keeping the temperature at 160°—180°C. Then, 40 parts (0.33 mole) of trihydroxymethylaminomethane were added, keeping the temperature at 180°C., allowed to further react

for 1 hour and, when the total amount of distillate water amounted to 27 parts (90% of the theoretical value), the flask and contents were cooled until the temperature had fallen to about 80°C., when xylene was added, to form an oily dispersoid of a nitrogen-containing high molecular weight calcium product XII of 60% concentration by weight.

Into this oily dispersoid of product XII, a dryer and solvent were added in accordance with Table 3, to form a non-pigmented rust-preventing paint.

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TABLE 3

	(parts)
Oily dispersoid of Product XII (solid matter 60%)	90.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	4.5
Xylene	4.5
	<u>100.0</u>

## EXAMPLES 13 — 22

Using the same procedure as described in Example 12, substituting stoichiometrical equivalent amounts of the various metal compounds shown in Table 4 for the calcium hy-

droxide, other oily dispersoids of nitrogen-containing high molecular weight reaction products were obtained, which were then incorporated in other non-pigmented rust-preventing paints.

TABLE 4

Example	Reactive Metal Compound	Nitrogen-containing High Molecular Weight Reaction Product	Blending Amount (parts)	Total Amount or Distillate Water (parts)
13	Cobalt hydroxide	Product XIII	31.6	27.0
14	Zinc hydroxide	Product XIV	33.8	27.0
15	Iron hydroxide	Product XV	36.3	33.0
16	Manganese hydroxide	Product XVI	30.2	27.0
17	Nickel hydroxide	Product XVII	31.5	27.0
18	Magnesium hydroxide	Product XVIII	19.8	27.0
19	Barium hydroxide	Product XIX	58.2	27.0
20	Cadmium hydroxide	Product XX	49.8	27.0
21	Strontium hydroxide	Product XXI	41.2	27.0
22a	Chromium hydroxide	Product XXIIa	35.0	33.0
22b	Lead oxide	Product XXIIb	76.0	21.0

- 5 A conventional rust-preventing paint consists of product XII of Example 12 was mixed with a long oil alkyd resin varnish (oil length 60% by weight, modified with soybean oil), together with the colouring pigment and extender shown in Table 5, the mixture was roller milled or ball milled and more dryer and solvent were added to give another pigmented rust-preventing paint, which is a mixture of 80% long oil alkyd resin and 20% oily dispersoid of product XII, containing iron oxide pigment.

TABLE 5

	(parts)
Red iron oxide	8.0
Calcium carbonate	45.0
Aluminium stearate	0.5
Oily dispersoid of Product XII (solid matter 60%)	7.0
Long oil alkyd resin varnish (solid matter 60%)	28.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	10.5
	100.0

- 15 EXAMPLES 24—33  
Following the procedure of Example 23, substituting the nitrogen-containing high molecular weight reaction products as shown in Table 6 for the oily dispersoid of product XII, other pigmented rust-preventing paints were made.

TABLE 6

Example	Reactive Metal Compound	Nitrogen-containing High Molecular Weight Reaction Product
24	Cobalt hydroxide	Product XIII
25	Zinc hydroxide	Product XIV
26	Iron hydroxide	Product XV
27	Manganese hydroxide	Product XVI
28	Nickel hydroxide	Product XVII
29	Magnesium hydroxide	Product XVIII
30	Barium hydroxide	Product XIX
31	Cadmium hydroxide	Product XX
32	Strontium hydroxide	Product XXI
33a	Chromium hydroxide	Product XXIIa
33b	Lead oxide	Product XXIIb

## EXAMPLE 34

- 336 parts (0.6 mole) of tall oil dimer acid and 112 parts (0.4 mole) of linseed oil fatty acid were placed in a three-necked flask with a stirrer, thermometer and condenser with branched tubes, heated for 30 minutes while stirring and, when the temperature of the contents had become 160°C., 37.1 parts (0.5 mole) of calcium hydroxide were added little by little and allowed to react for 1 hour, keeping the temperature at 160° — 180°C. Then, 16.2 parts (0.12 mole) of trimethylolpropane were added, while raising the temperature to 200°C., and allowed to react for 3 hours; when the total amount of distillate water had amounted to 24.5 parts (theoretical value), heating was stopped and the flask and contents were allowed to cool, until the temperature had fallen to about 80°C., when xylene was added to dilute the product to 60% by weight and obtain an oily dispersoid of high molecular weight calcium product XXIII.
- Using this oily dispersoid of product XXIII, following the procedure of Example 1, the pigmented rust-preventing paint shown in Table 7 was preferred.

TABLE 7

	(parts)
Red iron oxide	8.0
Heavy calcium carbonate	48.0
Oily dispersoid of Product XXIII (solid matter 60%)	39.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	4.0
	<hr/> 100.0

## EXAMPLES 35 — 44

- Following the procedure of Example 34, but substituting, for the 37.1 parts (0.5 mole) of calcium hydroxide, the metal compounds shown in Table 8, pigmented rust-preventing paints were prepared as set out below.

TABLE 8

Example	Reactive Metal Compound	High Molecular Weight Reaction Product	Blending Amount (parts)	Total Amount of Distillate Water (parts)
35	Cobalt hydroxide	Product XXIV	46.5	24.5
36	Zinc hydroxide	Product XXV	49.7	24.5
37	Iron hydroxide	Product XXVI	53.4	33.5
38	Manganese hydroxide	Product XXVII	44.5	24.5
39	Nickel hydroxide	Product XXVIII	46.4	24.5
40	Magnesium hydroxide	Product XXIX	29.2	24.5
41	Barium hydroxide	Product XXX	85.7	24.5
42	Cadmium hydroxide	Product XXXI	73.2	24.5
43	Strontium hydroxide	Product XXXII	60.8	24.5
44a	Chromium hydroxide	Product XXXIIIa	51.5	33.5
44b	Lead oxide	Product XXXIIIb	111.6	15.5

## EXAMPLE 45

98 parts (1 mole) of maleic anhydride and 280 parts (1 mole) of linseed oil fatty acid were placed in a three-necked flask with a stirrer, thermometer and condenser provided with branched tubes, and the mixture was heated to 200°C. in about 30 minutes, allowed to react for about 5 hours and, after the temperature had fallen to 160°C., 37.1 parts (0.5 mole) of calcium hydroxide were added little by little, allowed to react for about 1 hour at 160° — 180°C. while stirring, then 32 parts (0.27 mole) of trimethylethane were added

little by little, keeping the temperature at 180°C., allowed to react for 1 hour and, when the total amount of distillate water amounted to 32.5 parts, heating was discontinued and the flask and contents were allowed to cool; when the temperature had fallen to 80°C., xylene was added to produce an oily dispersoid of high molecular weight calcium product XXXIV of 60% concentration by weight.

Using this oily dispersoid of product XXXIV, following the procedure of Example 1, pigmented rust-preventing paints as shown in the following Table 9 were prepared.



TABLE 9

	(parts)
Iron oxide	9.0
Heavy calcium carbonate	48.0
Oily dispersoid of Product XXXIV (solid matter 60%)	39.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	3.0
	<hr/> 100.0

## EXAMPLES 46—55

Following the procedure of Example 45, but instead of 37.1 parts (0.5 mole) of calcium hydroxide, using 0.5 mole of the respective metal compounds shown in Table 10, other pigmented rust-preventing paints have been prepared.

TABLE 10

Example	Reactive Metal Compound	High Molecular Weight Reactive Product	Blending Amount (parts)	Total Amount of Distillate Water (parts)
46	Cobalt hydroxide	Product XXXV	46.5	32.5
47	Zinc hydroxide	Product XXXVI	49.7	32.5
48	Iron hydroxide	Product XXXVII	53.4	41.5
49	Manganese hydroxide	Product XXXVIII	44.5	32.5
50	Nickel hydroxide	Product XXXIX	46.4	32.5
51	Magnesium hydroxide	Product XL	29.2	32.5
52	Barium hydroxide	Product XLI	85.6	32.5
53	Cadmium hydroxide	Product XLII	73.2	32.5
54	Strontium hydroxide	Product XLIII	60.8	32.5
55a	Chromium hydroxide	Product XLIVa	51.5	41.5
55b	Lead oxide	Product XLIVb	111.6	13.0

## EXAMPLE 56

- 560 parts (1 mole) of tall oil dimer acid and 302 parts (1 mole) of rosin acid were placed in a three-necked flask with a stirrer, thermometer and condenser provided with branched tubes, heated for about 30 minutes and, when the temperature had become 160°C., 34.1 parts (0.46 mole) of calcium hydroxide were added little by little while stirring, and allowed to react for about 1 hour, keeping the temperature at 160°—180°C. Then, 53 parts (0.44 mole) of tris-hydroxymethylaminomethane were added, keeping the temperature at 180°C. and allowed to react for 1 hour and, when the total amount of distillate water amounted to 36 parts (90% of the theoretical value), heating was stopped and, when the temperature had fallen to 80°C., xylene was added to produce the desired oily dispersoid of nitrogen-containing high molecular weight calcium product XLV of 60% concentration.
- This oily dispersoid of product XLV was compounded with a drier and solvent as shown in Table 11, to produce a non-pigmented rust-preventing paint of the invention.

TABLE 11

	(parts)
Oily dispersoid of Product XLV (solid matter 60%)	90.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
xylene	9.0
	<hr/> 100.0

## EXAMPLES 57 — 66

- Following the procedure of Example 56, using, instead of 34.1 parts (0.46 mole) of calcium hydroxide, 0.46 mole of the respective metal compounds shown in Table 12, other non-pigmented rust-preventing paints were made.

TABLE 12

Example	Reactive Metal Compound	High Molecular Weight Reaction Product	Blending Amount (parts)	Total Amount of Distillate Water (parts)
57	Cobalt hydroxide	Product XLVI	42.8	36
58	Zinc hydroxide	Product XLVII	44.7	36
59	Iron hydroxide	Product XLVIII	49.2	44
60	Manganese hydroxide	Product XLIX	40.0	36
61	Nickel hydroxide	Product L	42.8	36
62	Magnesium hydroxide	Product LI	26.8	36
63	Barium hydroxide	Product LII	78.7	36
64	Cadmium hydroxide	Product LIII	67.4	36
65	Strontium hydroxide	Product LIV	55.7	36
66a	Chromium hydroxide	Product LVa	47.4	44
66b	Lead oxide	Product LVb	102.0	28

## EXAMPLE 67

5 630 parts (1.12 moles) of tall oil dimer acid were placed in a three-necked flask with a stirrer, thermometer and condenser provided with branched tubes, heated for 30 minutes while stirring and, when the temperature rose to 160°C., 19.1 parts (0.34 mole) of calcium oxide were added little by little and allowed to react for 1 hour, keeping the temperature at 160°—180°C. Then, 40 parts (0.33 mole) of tris-hydroxymethylaminomethane were added, keeping the temperature at 180°C., allowed to react for 1 hour and, when the total amount of distillate water amounted to 21.5 parts (90% of the theoretical value), the temperature of the reaction product was allowed to fall

to about 80°C. and xylene was then added, to produce a nitrogen-containing oily dispersoid of high molecular weight calcium product LVI of 60% concentration by weight.

This oily dispersoid of product LVI was then mixed with long oil alkyd resin varnish (oil length 60%, modified with soybean oil), and compounded with colouring pigments and extender as shown in Table 13, using roller milling or ball milling and then with a dryer and a solvent, to form a pigmented rust-preventing paint, containing a mixture of 80% by weight long oil alkyd resin varnish and 20% by weight oily dispersoid of product LVI.

TABLE 13

	(parts)
Red iron oxide	8.0
Calcium carbonate	45.0
Aluminium stearate	0.5
Oily dispersoid of Product LVI (solid matter 60%)	7.0
Long oil alkyd resin varnish (solid matter 60%)	28.0
Lead naphthenate (Pb: 15%)	0.8
Cobalt naphthenate (Co: 5%)	0.2
Mineral spirit	10.5
	100.0

## EXAMPLES 68—73

Following the procedure of Example 67, using, instead of 19.1 parts (0.34 mole) of cal-

cium oxide, the respective metal oxides of Table 14, other pigmented rust-preventing paints of the invention were obtained. 5

TABLE 14

Example	Reactive Metal Compound	Nitrogen-containing High Molecular Organometallic Compound	Blending Amount (parts)	Total Amount of Distillate Water (parts)
68	Cobalt oxide	Compound LVII	25.5	21.5
69	Zinc oxide	Compound LVIII	27.6	21.5
70	Manganese oxide	Compound LIX	53.8	26.5
71	Magnesium oxide	Compound LX	13.7	21.5
72	Barium oxide	Compound LXI	52.0	21.5
73	Strontium oxide	Compound LXII	31.4	21.5

10 The above-mentioned Examples 1 — 73 of the invention, wherein oily dispersoids of high-molecular reaction products are used, maybe compared with the formulae of Reference

Compositions, wherein JIS indicates those which comply with Japanese Industrial Standards.

## REFERENCE 1

## Oily LEAD Red Rust-Preventing Paint (JIS K 5622—1)

	(parts)				
Red lead ( $\text{Pb}_3\text{O}_4$ 98%)	..	..	..	..	79.0
Zinc oxide	..	..	..	..	1.0
Aluminium stearate	..	..	..	..	0.5
Processed drying oil	..	..	..	..	18.0
Manganese naphthenate (Mn: 5%)	..	..	..	..	0.2
Mineral spirit	..	..	..	..	1.3
					<u>100.0</u>

## REFERENCE 2

Oily Iron Oxide Rust-Preventing Paint (JIS K 5621—1)  
(General Use)

	(parts)				
Red iron oxide	..	..	..	..	8.0
Zinc oxide	..	..	..	..	8.0
Calcium carbonate	..	..	..	..	47.0
Aluminium stearate	..	..	..	..	0.5
Processed drying oil	..	..	..	..	30.0
Lead naphthenate (Pb: 15%)	..	..	..	..	0.8
Manganese naphthenate (Mn: 5%)	..	..	..	..	0.2
Mineral spirit	..	..	..	..	5.5
					<u>100.0</u>

## REFERENCE 3

Long Oil Alkyd Resin Red Lead Rust-Preventing Paint  
(JIS K 5622—2)

	(parts)
Red Lead ( $Pb_3O_4$ 98%) .. .. .	64.0
Zinc oxide .. .. .	2.0
Aluminium stearate .. .. .	0.5
Long oil alkyd resin varnish (solid matter 60%) (oil length 60%, modified with soybean oil) .. .. .	24.0
Lead naphthenate (Pb: 15%) .. .. .	0.8
Cobalt naphthenate (Co: 5%) .. .. .	0.2
Mineral spirit .. .. .	8.5
	<hr/> 100.0

## REFERENCE 4

## Long Oil Alkyd Resin Clear Paint

	(parts)
Long oil alkyd resin varnish (solid matter 60%) (oil length 60%, modified with soybean oil) .. .. .	90.0
Lead maphthenate (Pb: 15%) .. .. .	0.8
Cobalt naphthenate (Co: 5%) .. .. .	0.2
Mineral spirit .. .. .	9.0
	<hr/> 100.0

Test results obtained with these Examples in comparison with the Reference Compositions are shown as follows:

- 5 Test plate 1 is a steel plate, from which not all rust has been removed;

Test Plate 2 is a steel plate, completely freed from rust by sandblasting;

- 10 Test plate 3 is a non-rused polished mild steel plate, cleaned by polishing.

- 15 These plates were respectively coated twice to uniform thickness at an interval of 24 hours by brushing on with the above-mentioned rust-preventing paints, after allowing them to stand in a room for 7 days, and then exposed to the atmosphere, for 6 months after treatment with the non-pigmented paint and for 8

months with the pigmented paint.

## TEST EXAMPLE

Non-pigmented paint, oily dispersoid of nitrogen-containing high molecular weight reaction product used singly.

In the following Test Examples, "Sello-tape" is a Trade Mark for adhesive tape and the symbols used to denote rust-preventing effect have the following meanings:

e=excellent  
g=good  
f=fair  
rp=rather poor  
p=poor

20

25

30



Test item \ No. of Test piece			Example										Reference		
			47	48	49	50	51	52	53	54	55a	55b	1	2	3
Atmospheric exposure, coated twice (8 months)	Test plate 1	Appearance (rust, scab)	e	e	e	e	e	e	e	e	e	e	rp	rp	p
	Test plate 2	Appearance (rust, scab)	e	e	e	e	e	e	e	e	e	e	g	g	g
		Square cut sello-tape test	e	e	e	e	e	e	e	e	e	e	rp	rp	rp

## TEST EXAMPLE 3

Pigmented paint, in which a vehicle prepared by admixing long oil alkyd resin varnish with an oily dispersoid of a nitrogen-containing high molecular weight reaction product is used.

Test item \ No. of Test piece			Example												
			23	24	25	26	27	28	29	30	31	32	33a	67	33b
Atmospheric exposure, coated twice (8 months)	Test plate 1	Rust preventing effect	e	e	e	e	e	e	e	e	e	e	e	e	e
		Square cut sello-tape test	e	e	e	e	e	e	e	e	e	e	e	e	e

Test item \ No. of Test piece			Example						Reference	
			68	69	70	71	72	73	3	
Atmospheric exposure, coated (8 months)	Test plate 1	Rust preventing	e	e	e	e	e	e	p	
		Square cut sello-tape test	e	e	e	e	e	e	rp	

As it is clear from the results of Test Examples 1—3, because the rust-resisting paint of the invention is composed of film-forming material containing a high molecular weight metal containing reaction product which has a carboxyle group terminating its structure, it readily wets and permeates the surface of steel which is still rusty due to insufficient surface treatment; furthermore, the rust-preventing paint of this invention adheres well to the steel surface, the rust on which was previously removed sufficiently and a film of which after coating has excellent characteristics such that

the coated steel surface can be maintained in a state free from corrosion, even in polluted air.

## WHAT WE CLAIM IS:—

1. A rust-preventing paint comprising a film forming high molecular weight metal containing reaction product having a carboxyl group terminating its structure the reaction product being obtained by reacting a metal-containing polycarboxylic acid having free carboxyl groups and an acid value of 50 to 300 with polyhydric alcohol in an amount stoichiometrically less than



the carboxyl groups present in the metal containing polycarboxylic acid, which is itself obtained by reacting an aliphatic polycarboxylic acid having free carboxyl groups with a  
5 hydroxide or oxide of lead, calcium, cobalt, zinc, iron, manganese, nickel, magnesium, barium, cadmium, strontium or chromium in an amount stoichiometrically less than the carboxyl groups present in said aliphatic polycarboxylic acid.  
10 2. A rust-preventing paint according to claim 1, in which the metal-containing polycarboxylic acid is obtained by reacting less than a stoichiometrically equivalent amount of  
15 a reactive metal hydroxide or oxide with the

carboxyl groups present in the polycarboxylic acid or a mixture of the polycarboxylic acid and a stoichiometrically equivalent amount or less of a monocarboxylic acid.

3. A rust-preventing paint according to any preceding claim, containing pigments and/or other additives as hereinbefore defined.

4. A rust-preventing paint according to claim 1, substantially as hereinbefore described.

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